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BAYER CORPORATION

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**Central Division for Patents,
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Thermoplastic Polyurethane Elastomers

with improved processability

The current invention concerns new thermoplastic polyurethanes, their production as well as application in the manufacturing of formed bodies by injection molding, extrusion or calendering, as well as for coating materials in the broadest sense. Thermoplastic polyurethane elastomers have long been known; for example, they are extensively described in the "Kunststoffhandbuch" [Plastics Handbook], volume VII, by Vieweg-Höchtlen, Carl Hanser publishing company. Polyurethane elastomers of this type can be fashioned into their final shape by subsequent forming (injection molding, extrusion, calendering). Thermoplastic processability represents a great technical advance as compared to earlier known processing methods by pouring and casting, because they render the production of small forms economical. On the other hand, problems have been encountered up to now in the manufacturing of large forms with complex contours or of forms with thin wall thickness, because the high viscosity and limited flowability of the polyurethane melts prevent the form from being totally filled. Therefore, experiments were conducted in order to obtain a low viscosity of the thermoplastics by increasing the temperatures at which processing was done.

However, increasing the processing temperature leads to the appearance of combustion and disintegration phenomena in the material: bubbles, shrinking, streaking and other undesirable characteristics such as stickiness appear in the injection molds. Even the production of thermoplastically processable polyurethane raw materials in the form of granulates has proven to be extremely difficult up until now: thermoplastic polyurethane elastomers with high mechanical strength levels can only be produced within a very narrow range of the NCO/OH ratio, for which a highly precise quantitative measurement is required as well as a very accurate monitoring of the processing temperature during the production process. However, in this very narrow range of the NCO/OH ratio, a very close molecular weight distribution is obtained, and with it, a very narrow melting range of the polymer. Therefore, very accurate monitoring of the temperature is required for thermoplastic processing, because the slightest fluctuations in temperature will affect quality to the detriment of the final product or formed body.

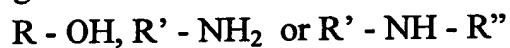
Surprisingly enough, it was discovered that the presence of relatively low quantities of primary alcohols, such as the presence of primary and secondary amines during chain elongation, leads to polyurethanes, which can easily be reproduced within a broad NCO/OH ratio, which can be processed within a broader temperature range and beyond this, which even exhibit improved flowability and thus make it possible to produce large formed bodies with complicated contours or even forms with thin wall thicknesses as well. The improved flowability lowers energy consumption during processing, because the granulates are more quickly melted up in the plasticizing form of the processing machine. Due to the even rapid melting of the granulates, improved homogeneity is achieved for the melts, such that the

finished formed bodies do not exhibit any streaking from flowing and have an excellent surface finish shine. Another advantage of the polyurethane in accordance with the invention is that the formed bodies cling less tightly to the molds; mold releasing agents are therefore not required in subsequent processing which translates into savings. Furthermore, the addition of lubricating waxes can be reduced. In addition, there is a better tolerance of lubricating agents which means a reduction in the unsightly formation of wax films on the surface of the formed bodies. Owing to the improved lubricating effect of the new polyurethane elastomers, the danger of destroying freshly formed articles during opening and release of the mold is reduced in an advantageous manner.

In the Belgian Patent no. 799 408, the production of polyurethanes with very close molecular weight distribution under concurrent use of preferably sterically hindered secondary alcohols is described. The secondary alcohols react toward the end of the chain elongation reaction with excess isocyanate groups by chain breaking and thus permit the production of polyurethane macromolecules with the most accurately definable molecular weight. The task set forth by the Belgian patent no. 799 408 is precisely diametrically opposed to the task set forth by the current invention, because in accordance with this invention, polyurethanes are to be produced with a broad spectrum in the distribution of molecular weights.

In analogy, in the US Patent Specification 3 718 622, a long chain, monofunctional, ester group containing alcohol, preferably from isobutyric acid monoester of 2,2,4 - trimethyl pentanediol - 1,3, is concurrently used for the production of polyurethane elastomers. Let it be expressly pointed out, that such a long chain ester alcohol is very slow to react. Therefore it does not react like the chain terminators to be added in accordance with the invention at the beginning of the poly-addition reaction with part of the diisocyanate present by broadening the scope of molecular weights, but it reacts rather like the secondary alcohols in the Belgian patent no. 799 408 toward the end of the chain elongation reaction with the excess isocyanate still present then. The polyurethanes in US Patent Specification 3 718 622 therefore also exhibit a relatively close molecular weight distribution.

The subject of the current invention are thermoplastic polyurethane elastomers of polyalcohols with molar weights between 800 and 5,000, diisocyanates, chain elongating dihydric alcohols with molar weights under 500, and with 0.003 mole to 0.08 moles per mole of chain elongating dihydric alcohol of a monofunctional chain terminator with the general structural formula:



whereby R, R' and R'' signify a straight or branched hydrocarbon chain with 1 to 30 carbon atoms, which possibly can contain oxygen, sulfur or other heteroatoms, and the total ratio of $NCO / (OH + NH)$ lies between 0.96 and 1.08, preferably between 0.98 and 1.06.

Furthermore, the subject of the current invention is a one step or multiple step process for the production of thermoplastic polyurethane elastomers from polyhydric alcohols with molar weights between 800 and 5,000, with chain elongating dihydric alcohols with molar weights under 500, and with diisocyanates, which is thus characterized in that a primary monofunctional alcohol with the formula $R - OH$ and/or a primary or secondary amine with the formula $R' - NH - R''$ at a moiety of 0.003 to 0.08 moles per mole of chain elongator is/are simultaneously added in together with the chain elongator, and that the equivalent ratio between all NCO- and NH- or OH-groups present amounts to between 0.96 and 1.08.

Furthermore, the invention concerns the use of thermoplastic polyurethane elastomers, as defined above, for the production of preforms according to the processes of injection molding, extrusion or calendering.

Furthermore, in their dissolved form, the thermoplastic polyurethane elastomers in accordance with the invention are also suited for coating of substrates, impregnation of textiles and for gluing multiple layers together.

The primary monofunctional alcohols used in accordance with the invention are straight chain or branched chain alkanols with 1 - 30, preferably 1 - 12, especially preferred 6 - 8, carbon atoms, which possibly also contain heteroatoms, such as e.g. oxygen and sulfur, but which are free of carbonyl groups. Examples of such would be butanol, hexanol, octanol,

isooctanol, nonyl alcohol, decyl alcohol, dodecyl alcohol and stearyl alcohol. Very suitable primary monofunctional alcohols are ethylene glycol mono-alkyl ethers also, such as for example, ethylene glycol mono-methyl ether or ethylene glycol mono-ethyl ether.

By monofunctional primary alcohols in the sense of the current invention we also mean to include alkoxylation products of monofunctional alcohols, for example the addition product of ethylene oxide to butylene glycol.

As chain terminators in the sense of the invention, monofunctional aliphatic amines with the general formula $R' - NH^2$ and/or $R' - NH - R''$ are also included. R' and R'' stand for straight or branched aliphatic hydrocarbon chains, which can also possibly contain oxygen, sulfur or other heteroatoms. R' contains 1 to 30, preferably 1 - 18 carbon atoms; R'' is a radical with 1 to 30, preferably 1 to 12 carbon atoms. Named as examples for such amines are butyl amine, hexyl amine, 2 - ethyl hexyl amine, dodecyl amine, stearyl amine, dibutyl amine, dinonyl amine, bis - (2 - ethyl hexyl) - amine and N-methyl stearyl amine.

As starter components for the production of thermoplastic polyurethane elastomers in accordance with the invention, aliphatic, cyclo-aliphatic and aromatic diisocyanates come under consideration as they are described by W. Siefgien in Justus Liebig's "Annals of Chemistry", 562, pages 75 - 136; for example:

ethylene diisocyanate, 1,4 - tetra-methylene diisocyanate, 1,6 - hexa-methylene diisocyanate, 1,12 - dodecane diisocyanate, cyclobutane - 1,3 - diisocyanate, cyclohexane- 1,3 - and - 1,4 -diisocyanate, as well as random mixtures of these isomers, 1- isocyanato - 3,3,5 - trimethyl - 5 - isocyanato - methyl - cyclohexane (German Patent Application DAS 1 202 785), 2,4 - and 2,6 - hexahydro - toluylene - diisocyanate, as well as random mixtures of these isomers, hexahydro - 1,3- and/or - 1,4 - phenylene - diisocyanate, perhydro - 2,4'- and/or - 4,4' - diphenyl methane - diisocyanate, 1,3 - and 1,4 - phenylene diisocyanate, 2,4 - and 2,6 - toluylene diisocyanate, as well as random mixtures of these isomers, diphenyl methane - 2,4' - and/or - 4,4' - diisocyanate, naphthylene - 1,5 - diisocyanate.

Especially preferred are poly-isocyanates, that are usually easily available in the industry, such as 2,4 - and 2,6 - toluylene diisocyanate as well as mixtures thereof, diphenyl methane diisocyanate, 4,4' - diisocyanato - dicyclo- hexyl methane, as well as 1,6 - diisocyanato hexane.

Coming under consideration for the process in accordance with the invention are higher molecular polyalcohols, for example polyesters exhibiting hydroxyl groups, in particular transformation products of dihydric alcohols with divalent carboxylic acids. Instead of the free dicarboxylic acids, the corresponding carboxylic acid anhydrides or corresponding carboxylic acid esters from low alcohols, or mixtures thereof, can also be used for the production of polyesters. The dicarboxylic acids can be of aliphatic, cycloaliphatic, aromatic and/or heterocyclic nature, and possibly be substituted by halogen atoms for example, and/or be unsaturated. As examples for this, we name a few: succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, phthalic anhydride, tetrahydro phthalic anhydride, hexahydro phthalic anhydride, tetrachloro phthalic anhydride, endomethylene tetrahydro phthalic anhydride, glutaric anhydride, maleic acid, maleic anhydride, fumaric acid, dimethyl terephthalate and terephthalic acid - bis - glycol ester. As dihydric alcohols, for example, the following come into question: ethylene glycol, propylene glycol - (1,2) and - (1,3), butylene glycol - (1,4) and - (2,3), hexanediol - (1,6), octanediol - (1,8), neopentyl glycol, cyclohexane dimethanol (1,4 - bis - hydroxy methyl cyclo hexane), 2 - methyl - 1,3 - propanediol, furthermore diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, dipropylene glycol, polypropylene glycol, dibutylene glycol and polybutylene glycols. The polyesters can exhibit shared end position carboxyl groups. Even polyesters from lactones can be used such as for example, γ - caprolactone or hydroxy carboxylic acids, e.g., T - hydroxy caproic acid.

The polyethers under consideration, preferably exhibiting two hydroxyl groups in accordance with the invention, are such that are already known and are represented, for example, by polymerization of epoxides such as ethylene oxide, propylene oxide, butylene oxide, tetra hydrofuran, styrene oxide or epichlorohydrin with itself/themselves, e.g. in the presence of BF_3 , or by addition reaction of these epoxides, possibly into a mixture or possibly by sequential addition to starter components with highly reactive hydrogen atoms such as alcohols or amines, e.g., water, ethylene glycol, propylene glycol - (1,3) or - (1,2), 4,4' - dihydroxy diphenyl propane, aniline, ethanolamine or ethylene diamine. Polyethers that are modified by vinyl polymerizates, for example such as those developed by polymerization of styrene or acrylic nitrile in the presence of polyethers, are equally suitable (see American Patents 3,383,351, 3,304,273, 3,523,093, 3,110,695, and German Patent 1,152,536), as well as are polybutadienes exhibiting OH groups.

Trifunctional polyethers at moieties of 0 to 30 weight%, relative to bifunctional polyether, can also be added. As starters for these polyethers, glycerin and trimethylol propane can be used among other things. Polymerization is carried out with the epoxides mentioned above.

Among the polythioethers, the condensation products of thiodiglycol with itself and/or with other glycols, with dicarboxylic acids, formaldehyde, amino carboxylic acids or amino alcohols should be listed in particular. Depending on the co-components, the products we are dealing with here are mixed polythioethers, polythioether esters or polythioether ester amides.

As polyacetals, compounds come under consideration which can be produced, for example, from glycols, such as diethylene glycol, triethylene glycol, 4,4' - dioxethoxy diphenyl dimethyl methane, hexanediol and formaldehyde. Polyacetals suitable for the process in accordance with the invention can also be produced by the polymerization of cyclic acetals.

As polycarbonates exhibiting hydroxyl groups, such come under consideration that are known and can be produced, for example, by transformation of dihydric alcohols such as propandiol- (1,3), butanediol- (1,4) and/or hexanediol- (1,6), diethylene glycol, triethylene glycol, tetraethylene glycol with diaryl carbonates, e.g. diphenyl carbonate.

Further representatives of higher molecular polyhydric alcohols to be used in accordance with the invention are described for example in "High Polymers", volume XIV, "Polyurethanes, Chemistry and Technology", compiled by Saunders-Frisch, Interscience Publishers, New York, London, volume I, 1962, pages 32 - 42 and pages 44 - 54, and volume II, 1964, pages 5 - 6 and 198 - 199, as well as "Kunststoff Handbuch" [Plastics Handbook], volume VII, Vieweg-Höchtlen, Carl-Hanser Publishers, Munich, 1966, e.g., on pages 45 through 71.

As chain elongating dihydric alcohols with molar weights below 500 for example, the compounds mentioned above for the production of polyesters come under consideration; preferred are ethylene glycol, diethylene glycol, butanediol, hexanediol, octanediol, decanediol and dodecanediol, as well as hydroquinone - \exists - dihydroxy - ethyl ether. Given the case, cross-linking agents with secondary OH- groups can also be present.

As a rule, when carrying out the process in accordance with the invention, stoichiometric relationships are met between the NCO- and OH- groups. While without the addition of monofunctional amines or primary alcohols, the characteristics of the obtained products are highly dependent on the NCO / OH - ratio, a consistently high quality product is obtained by the addition, in accordance with the invention, of primary and/or secondary amines and/or primary monofunctional alcohols in the range of an NCO / OH - ratio of about 0.96 to 1.08.

In general, for 1 mole of higher molecular polyhydric alcohol (preferably of a polyester or polyether), 1 to 12 moles of chain elongating dihydric alcohol as well as the corresponding quantity of diisocyanate (2 to 13 moles) are used. In addition, 0.003 to 0.08 moles, preferably 0.005 - 0.04 moles of monofunctional amine and/or primary alcohol are applied for each mole of chain elongating dihydric alcohol in accordance with the invention process.

The transformation of the reaction partners can be conducted according to the known one shot process. For this, temperatures of generally in between 70 and 170°C are maintained during mixing of the reaction partners.

If, however, the process in accordance with the invention is conducted according to the two shot process (prepolymer process), then the polyether and/or polyester and diisocyanate are prereacted first at between 50 to 150°C and subsequently transformed at temperatures between 70 and 150°C with the mixture composed of chain elongators and monofunctional alcohol or amine.

The process in accordance with the invention can also be conducted in the presence of lubricants, catalysts, anti-oxidants and similar auxiliary agents. Such lubricants are, for example, waxes, esters or amides of fatty acids, or derivatives of polyethylene. Suitable catalysts are, for example, tin (II) salts of carboxylic acids, tin (II) acetate, tin (II) octoate, tin (II) ethyl hexoate and the dialkyl tin salts of carboxylic acids, such as, for example, dibutyl tin diacetate or dibutyl tin dilaurate. Further representatives of useful catalysts as well as detailed information on their manner of reaction are described for example in the "Plastics Handbook", volume VII, compiled by Vieweg-Höchtlen, Carl-Hanser Publishers,

Munich 1966, on pages 96 to 102. Auxiliary agents such as hydrolysis inhibitors (e.g. carbodiimide) and antioxidants, such as sterically hindered phenols can also be used concurrently, of course. Filling agents can also be added such as carbon black, chalk, barium sulfate, kaolin or amorphous hydrated silica.

The transformation of the reaction partners is conducted in a known manner with known equipment. Continuous production, in which the reaction partners are introduced by means of dosing pumps into a mixing device, where they are homogeneously mixed together, provides especially satisfactory results. If the reacting mixture from this mixing device is transferred on to heated plates or conveyors that are possibly set up with releasing agents/lubricants, this proves to be especially advantageous. Of course, the reaction can also be conducted in a continuously operating kneading device.

By the addition of monofunctional primary and/or secondary amines and/or primary alcohols, in accordance with the invention, the flowability or the viscosity of the thermoplastic melts is favorably influenced. In particular, as already mentioned above, a consistent viscosity is targeted over a relatively broad NCO / OH ratio. This is illustrated in figure 1, in which "curve a" represents a conventional system, in which processing was done without the addition of a primary alcohol or amine; "curve b" shows that when adding octanol - 1 within an index range of 0.97 to 1.07, a practically consistent melt viscosity is obtained (expressed here by the melt index). The more elevated position of the melt index for "curve b" expresses the fact that polyurethane elastomers in accordance with the invention demonstrate an improved flowability, i.e., a lower viscosity. From this measured result, a

greater temperature span during processing, a lower energy consumption for the processing machine and an improved homogeneity of the final products can be expected. Comparative trials with thermoplastic polyurethane elastomers of the conventional type and with thermoplastic polyurethane resins demonstrate this effect in the case of injection molding as well as extrusion processing.

While conventional thermoplastic resins provide optimal mold bodies only within a temperature range of $\pm 3^{\circ}\text{C}$, the elastomers in accordance with the invention provide optimal uniform injection molds at a temperature range of $\pm 10^{\circ}\text{C}$. The improved surface shine and the improved homogeneity of the produced finished parts are especially noticeable. It is also surprising, that the thermoplastic polyurethane resins produced in accordance with the invention process exhibit significantly improved strength on the convergence seam as compared to that of the prior state of the art.

If a primary alcohol or a primary and/or secondary amine with a long hydrocarbon chain is/are used as monofunctional chain terminator, then it will simultaneously act as an integrated inner lubricant/releasing agent. Such integrated inner lubricants will not "sweat out" to the surface of the finished parts and therefore do not threaten to disfigure the appearance of the finished parts. If lubricating waxes are applied in addition, then compatibility is improved by the integrated long chain alkyl radicals and the tendency to rise to the surface is reduced. Due to the special lubricating effect of the elastomers in accordance with the invention, the use of mold releasing agents can indeed be largely avoided.

The polyurethane elastomers in accordance with the invention are especially well suited for the production of large surface or complex mold parts. They are of special interest for the production of sport shoes, ski boots and shock absorbers in automotive vehicles.

Example 1)

100 weight parts of ethanediol - butanediol - adipic acid polyester with a molar weight of 2,000 (OH number is 56) are thoroughly mixed together with 22 weight parts of butanediol - 1,4 and 1.2 weight parts of n - octanol (0.037 mole relative to butanediol - 1,4). 0.3 weight parts of stearyl amide and 1 weight part of stabilizer (2,6, 2',6' - tetra isopropyl diphenyl carbodiimide) are yet added to this. The mixture is heated up to 90°C while being stirred and equivalent quantities of 4,4' - diphenyl methane diisocyanate (74.6 parts relative to total OH) are mixed in at 60°C under vigorous stirring. After this, the mixture is poured on a sheet. The solidified product is granulated and sprayed over.

8 trials were conducted with analog recipes and with an NCO / OH ratio of 0.96, 0.98 etc. up to 1.10 (trials 1 a - 1 h). In figure 1 b, the intrinsic melt index obtained from measuring in a capillary viscometer at 210°C is plotted on the index curve.

In order to determine the melt index (= "intrinsic melt index") independent of time, the plastic melt which has been heated up to a specified temperature is pressed through a channel (extrusion die) at a specified ratio between the diameter and the length, and at a specified pressure, and the extruded quantity is determined by weighing out in analogy to ASTM D 1238-65 as melt index. If one determines the melt index in this manner after various length periods of preliminary heating time and extrapolates with $t = 0$, then one obtains the intrinsic

melt index (a linear time dependency is always assumed for the melt index). This value is a constant, independent of the preliminary heating time for the respective material. The time independent melt index provides information as to what quantity of material would be extruded under predetermined test conditions after 0 minutes of preliminary heating time, if it were possible to heat the material up to the testing temperature in 0 minutes.

As a testing device for the polymers of the current patent application, an HKV 2000 model viscometer was used, from the Göttfert Company in Buchen, Odenwald (West Germany). The extrusion die in this device had a length of 15 mm, a diameter of 1.05 mm and a conical intake with an opening angle of 60°. The pressure on the melts amounted to 177.0 KP/cm².

If the same trials are repeated without the addition of chain terminators (trials 1 e - 1 p), then products are obtained with the values represented in figure 1. Upon comparing both figures, it becomes clear that in figure 1 b, trials 1 b and 1 f indicate a more or less consistent melt index of 20 to 30 in the index range of 0.98 - 1.06, while in figure 1 a the melt index fluctuates from 5 to 70 within the same index range. This means, that the characteristics can be adjusted to a level of consistency by the use of chain terminators (figure 1 b).

Based on testing and comparison of some of the products, the following mechanical values were also determined:

TRIALS

		l c	l k	l d	l l	l e	l m
Tensile strength (DIN 53 504)	KP/cm ²	476	380	515	510	505	480
Elongation at break (DIN 53 504)	%	450	420	460	440	435	430
Elasticity (DIN 52 512)	%	30	28	29	29	30	29
Flow spiral	cm	105	76	102	69	108	75
Processing width	°C	± 11	± 4	±10	± 3	±11	± 4
Surface	-	homogeneous	streaky	homogeneous	streaky	homogeneous	streaky

Torsional moment	MKP	4	8	3	9	3	10
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The flow spiral is a spiral shaped curved steel section with a half circle cross section (radius of the half circle: 4 mm) into which the thermoplastic material is injected. The extrusion conditions for this are the same as for the ejection of S 1 - rods according to DIN 53 504 (injection molding machine: Stübbe page 65): the cylinder temperature of the extrusion die amounts to 200°C; in the feed zone to about 200 - 220°C. Screw speed: 130 revolutions per minute; injection pressure: 630 KP/cm²; ramming pressure: 90KP/cm²; cycle 20 sec./20 sec. The half circle steel section is cooled with water in order to maintain a temperature of 40°C on the section face.

The measured value provided in the table is the distance from the injection point to the point where the thermoplastic resin presses forward into the flow spiral. Therefore, high measured values signify great thermoplasticity of the material.

The torsional moment was measured by an HKV 2000 type extrusion meter by the Göttfert Company (Buchen) during the extrusion of a granulate preannealed at 110°C for a period of 17 hours under the following conditions: a 20-D three zone screw was used with a compression of 1:3 and a speed of 30 revolutions per minute. Extrusion die diameter: 2 mm; yield: 55 g/min.; housing temperature from the feed zone to the metering ring zone: 200 - 210°C.

High measured values for the torsional moment are an indication of low thermoplasticity of the polyurethane subjected to testing.

Example 2

100 weight parts of polycaprolactonediol (OH number 56) are reacted with 10 parts of butanediol - 1,4, 0.09 parts of stearyl alcohol, 41.2 g of 4,4' - diphenyl methane diisocyanate (NCO / OH = 1.02) in accordance with the processing manner described above and are processed further (2a). Compared to the product without the addition of stearyl alcohol (trial 2 b), the following characteristics are obtained:

	Unit	Standard	2a	2b
Tensile strength	KP/cm ²	DIN 53 504	410	390
Elongation at break	%	DIN 53 504	620	580
Elasticity	%	DIN 53 512	48	46
Flow spiral	cm	-	105	80
Processing width	°C	-	± 7	±3
Torsional moment	MKP	-	2	4
Surface	-	-	homogeneous shiny	streaky

Example 3

100 weight parts of hexanediol polycarbonate (OH number is 56), 22 parts of butanediol - 1,4, 1.0 parts of n - butanol and 76.6 parts of 4,4' - diphenyl methane diisocyanate (NCO / OH = 1.02) are transformed as described in example 1 and further processed (3a).

Compared to an elastomer without the integration of n-butanol (3b), the following values are obtained:

	Unit	Standard	3a	3b
Tensile strength	KP/cm ²	DIN 53 504	420	380
Elongation at break	%	DIN 53 504	430	370
Elasticity	%	DIN 53 512	35	34
Flow spiral	cm	-	98	74
Processing width	°C	-	± 6	± 2

Torsional moment	MKP	-	4	8
Surface	-	-	homogeneous shiny	streaky

Example 4

50 weight parts of polypropylene glycol polyether with a molar weight of 2,000 and 55.9 weight parts of 4,4' - diphenyl methane diisocyanate are transformed at 100°C for one hour into a preliminary polymer. After this, a mixture of 50 weight parts of ethene dihydric alcohol adipic acid polyester with a molar weight of 2,000, 15 parts of butanediol - 1,4, 1 part of stearyl amide and 0.4 parts of ethylene glycol monomethyl ether (NCO / OH = 1.02) are heated up to 80°C and thoroughly mixed with the preliminary polymer. Reprocessing was conducted as in trial 1 (4 a). Once more, an elastomer was produced, without ethylene glycol monomethyl ether, by which to draw the comparison (4 b).

	Unit	Standard	4a	4b
Tensile strength	KP/cm ²	DIN 53 504	318	280
Elongation at break	%	DIN 53 504	450	420

Elasticity	%	DIN 53 512	39	37
Flow spiral	cm	-	119	82
Processing width	°C	-	± 11	± 4
Torsional moment	MKP	-	3	7
Surface	-	-	homogeneous shiny	streaky

Example 5

50 weight parts of poly-tetramethylene oxide ether (molar weight of 2,000), 50 weight parts of the same ether but with a molar weight of 1,000, 0.5 weight parts of bis-stearyl ethylene diamine, 12 weight parts of butanediol - 1,4, 1.5 weight parts of dodecyl alcohol and 53.9 weight parts of 4,4' - diphenyl methane diisocyanate (NCO / OH = 1.02) are transformed as described in example 1 (5 a). For comparison, a batch was produced without dodecyl alcohol (5 b).

	Unit	Standard	5a	5b
Tensile strength	KP/cm ²	DIN 53 504	400	360
Elongation at break	%	DIN 53 504	550	520
Elasticity	%	-	45	44
Flow spiral	cm	-	122	79
Torsional moment	MKP	-	4	8
Surface	-	-	homogeneous shiny	homogeneous
Processing width	°C	-	± 10	± 4

Example 6

100 weight parts of ethylene glycol adipic acid polyester (molar weight of 2,000), 26 weight parts of butanediol 1,4, 1.17 weight parts of 2 - ethyl hexyl amine and 87.6 parts of 4,4' - diphenyl methane diisocyanate (NCO / OH = 1.03) are transformed as described in example 1 (6a) . For comparison, a batch was produced without 2 - ethyl hexyl amine (6 b).

	Unit	Standard	6a	6b
Tensile strength	KP/cm ²	DIN 53 504	510	480
Elongation at break	%	DIN 53 504	430	400
Elasticity	%	DIN 53 512	39	38
Flow spiral	cm	-	83	54
Processing width	°C	-	± 8	± 3
Torsional moment	MKP	-	4	10

Surface	-	-	homogeneous shiny	homogeneous
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Example 7

100 weight parts of butanediol adipic acid polyester (molar weight of 2,000), 26 weight parts of butanediol -1,4, 2.58 weight parts of methyl stearyl amine and 87.6 weight parts of 4,4' - diphenyl methane diisocyanate (NCO / OH = 1.03) are transformed as described in example 1 (7a). For comparison, a batch was produced without methyl stearyl amine (7b).

	Unit	Standard	7a	7b
Tensile strength	KP/cm ²	DIN 53 504	480	490
Elongation at break	%	DIN 53 504	460	420
Elasticity	%	DIN 53 512	37	35
Flow spiral	cm	-	102	64
Processing width	°C	-	± 9	± 3

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Torsional moment	MKP	-	4	9
Surface	-	-	homogeneous shiny	homogeneous

Patent Claims:

- 1) Thermoplastic polyurethane elastomers of polyhydric alcohols with molar weights between 800 and 5,000, diisocyanates, chain elongating dihydric alcohols with molar weights below 500 and 0.003 moles to 0.08 moles per mole of chain elongating dihydric alcohol of a monofunctional chain terminator with the general structural formula $R - OH$, $R' - NH_2$ or $R' - NH - R''$ whereby R, R', and R'' signify a straight or branched hydrocarbon chain with 1 - 30 carbon atoms, which can possibly contain oxygen, sulfur and other heteroatoms, and the total ratio of $NCO / (OH + NH)$ lies between 0.96 and 1.08.
- 2) Process for the production of thermoplastic polyurethane elastomers in accordance with claim 1, thus characterized in that in a first step, a preliminary adduct is produced from the higher molecular polyhydric alcohol and the diisocyanate, which is then reacted in a second processing step with a mixture from the chain elongating dihydric alcohol and the chain terminator.
- 3) Process for the production of thermoplastic polyurethane elastomers in accordance with claim 1, thus characterized in that the higher molecular polyhydric alcohol, the chain elongating dihydric alcohol, the chain terminator and the diisocyanate are brought to transformation in a reaction step with temperatures ranging from 70 to 170°C.

- 4) Application of thermoplastic polyurethane elastomers in accordance with claim 1 for the production of polyurethane formed bodies by injection molding, extruding or calendering.
- 5) Application of thermoplastic polyurethane elastomers in accordance with claim 1 for coating substrates, impregnating textiles or used as adhesive agents.

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[Refer to the 2 original graphs]

Figure 1a

Intrinsic melt index

NCO / OH

Version no. 1i 1j 1k 1l 1m 1n 1o 1p

Figure 1b

intrinsic melt index

NCO / OH

Version no. 1a 1b 1c 1d 1e 1f 1g 1h